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FINAL REPORT

Main Group Organometallic Chemistry

by

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November 8, 1995

Main Group Organometallic Chemistry

AASERT Award - Supplement to

"Inorganic Polymers and the Elimination-Condensation reaction

N-00014-90-J-1530

The goal of the AASERT Award was to attract new graduate students to do research on the organometallic compounds of the main-group elements. The project was successful as three graduate students were recruited to join the project. These students are making progress with their research and have prepared and characterized new gallium and/or indium compounds.

Name of Student	Date Graduate Study Initiated
Michael T. Mosscrop	August 1993
Eric S. Robirds	August 1994
James R. Gardinier	August 1994

The research project which has been initiated by Michael Mosscrop involves an investigation of the effects of the substituents on the cyclopentadienyl ring on the chemistry of compounds of the type R_2GaCp, $RGaCp_2$ and $GaCp_3$ (R = Me, Et; Cg = any substituted cyclopentadienyl moiety). These compounds are being investigated as potential precursors to the gallium(I) intermediate, GaCp. Earlier work by others in the research group demonstrated that low oxidation state species react with elemental phosphorus to form materials at unusually low temperature. For example, $In(C_5Me_5)$ reacts with P_4 to form InP at 125°C under OMCVD conditions. Thus, the goal is to determine if R_2GaCp type compounds decompose selectively and readily to form GaCp and then react with phosphorus to form materials such as GaP at significantly lower temperatures that those typically employed in OMCVD, i.e. 600-800°C. Mr. Mosscrop has prepared and fully characterized $Me_2Ga(C_5H_4Me)$, $Et_2Ga(C_5H_4Me)$ and $Ga(C_5H_4Me)_3$. The related compounds, $MeGa(C_5H_4Me)_2$ and $EtGa(C_5H_4Me)_2$ decomposed by ligand distribution reactions to form appropriate equilibrium mixtures of $R_2Ga(C_5H_4Me)$ (R = Me, Et) and $Ga(C_5H_4Me)_3$. Mr. Mosscrop's research is now progressing to the synthesis of compounds with more bulky substituents on the ring such as $SiMe_3$ and CMe_3. The goal of research is to understand the effects of ring substituents on the structure, properties, decomposition chemistry and reactivity patterns of compounds of the type R_2GaCp.

Mr. Eric S. Robirds is studying the chemistry R_2InCp compounds. The chemical properties of the indium compounds will then be related to the corresponding gallium compounds. Mr. Robirds has prepared and characterized $Me_2In(C_5H_5)$. The initial preparative route involved the elimination of CH_4 from $InMe_3$ and C_5H_6 at 120-150°C. The indium compound is significantly more difficult to prepare and handle than the gallium derivative as the $Me_2In(C_5H_5)$ is insoluble in all non-basic solvents (pentane, benzene, etc.) and is nonvolatile at temperatures below 110°C. These properties suggest more extensive and stronger C_5H_5 bridge bonding than in $Me_2Ga(C_5H_5)$ or in $Et_2Ga(C_5H_5)$. These gallium compounds prepared by earlier workers in the group are soluble in hydrocarbons and are volatile at room temperature. It is also significant that $Me_2In(C_5H_5)$ does not react with excess cyclopentadiene to form $MeIn(C_5H_5)_2$ or $In(C_5H_5)_3$. Thus, the syntheses of $Me_2In(C_5H_5)$ and $MeIn(C_5H_5)_2$ by metathesis reactions of Me_nInCl_{3-n} (n = 1,2) and LiC_5H_5 are being investigated currently.

The goal of the research by Mr. James Gardinier is to investigate the use of β-diketonate ligands for stabilizing low oxidation states of gallium and indium. Thus, Mr. Gardinier has learned how to handle air sensitive compounds by preparing $Me_2Ga(O_2C_3HR_2)$ (R = CH_3, t-Bu, CF_3), $(Me)(Cl)Ga(O_2C_3HR_2)$ and $(Mesityl)Ga[O_3C_3H(CF_3)_2]$. All compounds have been fully characterized by acceptable elemental analyses, cryoscopic molecular weight studies in benzene solution and ^1H NMR studies. The compound $(Mesityl)_2Ga[O_2C_3H(CF_3)_2]$ has been the subject of an X-ray structural study and has the expected six-membered chelate ring, GaO_2C_3. The chloroderivative $(Me)(Cl)Ga(O_2C_3HR_2')$ will serve as a starting point for the potential synthesis of derivatives with two different organic substituents or with a hydride ligand, $(Me)(R)Ga(O_2C_3HR_2')$ (R = t-Bu, CH_2CMe_3, C_5Me_5, H) or for the synthesis of a gallium(II) compound by a reduction reaction.

All three students are currently in good standing in the Ph.D. program and are making acceptable progress on their research.